Novel Electrolyte Energy Storage Systems

Investigators
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Abstract
We seek an approach to enable widespread deployment of grid-based storage by drastically lowering the cost of such a system. We are doing so by reexamining the fundamentals of flow battery technology and engaging in an effort in which the active redox couples, the materials that separate the couples, and the flow characteristics that dictate the rate of delivery are optimized, thereby allowing system-level solutions with high efficiency and with capital costs that are much lower than if each aspect of the system were optimized with the other aspects left unchanged. Informed by a deep understanding of fuel cell design, we are developing materials in concert with an understanding of the ultimate device behavior, and engineering electrodes that ensure high power per unit area, drastically lowering the cost per unit of power delivered.

Tin(IV) bromide is a promising candidate for flow batteries because both redox couples, Sn(IV)/Sn(II) and Br$_2$/Br$^-$, are dissolved in same solution, which eliminates concerns of cross contamination. With a view toward discovering ways to improve poor electrochemical reversibility of Sn(IV)/Sn(II), progress is being made toward a complete understanding of the mechanism of the Sn(IV)/Sn(II) redox reaction. We have detected the Sn(III) intermediate through electrochemical analysis methods, and estimated a rate constant for disproportionation of Sn(III). In related work, the first studies are underway of the electrochemistry of Sn(IV)Cl$_4$ liquid, both undiluted and in solution with another solvent, toward development of a metal halide liquid redox flow battery. Additional redox couples are also under investigation.

Introduction
Efficient, cost-effective energy storage is vital to the effort to fully integrate renewable power sources into the electric utility grid. While compressed-air and pumped-hydro storage plants hold the promise of large-scale economical storage, they both require special sites. To date, redox flow batteries (RFB) have shown promise, but are presently far too expensive to be effectively deployed. This research offers an integrated approach to identify new electrolyte systems and cell designs that allow drastic cost reductions (removing this key barrier) while maintaining the high efficiency and ease of operation that are the hallmarks of RFB systems. Our approach brings together expert researchers with skills in chemistry, material science and characterization, electrochemical engineering, and mathematical modeling. We will advance new materials and electrochemistry for RFB systems, optimize cell designs, and develop guidelines for scaling up to utility-scale configurations.
The requirements for large-scale electrical energy storage systems are quite different from existing battery systems. While batteries for portable and transportation applications place a premium on weight and volume, stationary energy storage systems have considerably less stringent requirements. Backup power systems support telecommunications and data centers, but are generally not expected to survive large numbers of charge/discharge cycles. Time-of-day pricing on the grid, mandates for renewable power sources, and the accompanying intermittency of those renewable sources are creating demand for electrical energy storage. Energy needs to be stored efficiently, and to accommodate several hours of continuous energy accumulation and release to the grid.

For flow battery systems, one can specify independently the size of the electrochemical reactor (power capacity) and the size of the storage tanks of the free-flowing electrolyte streams (energy capacity). The ability to deliver the active material to the electrode surface by convection ensures that one can bypass mass-transport limitations that curtail the energy density of conventional batteries with solid-phase active materials. We seek to identify new electrolyte systems and cell designs that we expect will allow drastic cost reductions while maintaining the high efficiency and ease of operation that are the hallmarks of RFB systems.

Background

Flow batteries have been cited as a potential for grid-based energy storage, optimized over a very different set of metrics from conventional portable or transportation batteries. Several companies are developing flow battery technology to improve both the efficiency and stability of the smart grid. In recent months, in addition to flow schemes in which the active material is comprised of dissolved species in solution, researchers have also proposed a slurry based configuration, and a liquid metal halide electrolyte, either of which could drastically increase energy content per unit volume.[1] We seek to understand the limitations of such systems, and use that to benchmark the required performance of electrolyte systems.

Results

Semi-solid flow cell

The semi-solid flow cell (SSFC) [1] represents the first reported application of lithium chemistries to the flow battery concept. It uses low volume fractions of active materials (20-25%) and carbon (0.5-2%) with no polymeric binder, creating slurries that can be flowed through the electrode chambers as in a typical flow battery. The SSFC provides the ease of manufacturing and the scalability of flow batteries along with energy densities approaching that of solid-state lithium-ion batteries. This project is intended to verify the SSFC concept and its electrochemical performance and to provide some insight into possible engineering concerns, especially the design of the electrodes and the rate capability of the battery.

To explore these engineering problems, we created a discharge model based on porous electrode theory.[2] The porous electrode model is modified [3] by separating the continuous solid phase into two phases, one consisting of active material particles and the other consisting of carbon, such that the volume fractions of these two solid phases can
be altered independently of each other. The coupled set of governing equations and boundary conditions are solved using a modified Newton-Raphson method in a MATLAB simulation environment. As of this time, the model is under development.

To provide parameters for the model and to verify the electrochemical performance of the SSFC, we have begun to create a variety of semi-solid suspensions and insert them into coin cells, instead of creating a flow cell as was done in [1]. Cyclic voltammetry can be done to validate the model and to verify the performance of the SSFCs reported in [1]. Electrochemical impedance spectroscopy can be done to provide important conductivity values, which can be used in the model and can be compared to lithium-ion batteries with higher amounts of solid materials. Currently, we have successfully created half-cells by using Viton rubber O-rings to contain the semi-solid suspensions. Although the cells exhibit the correct open-circuit potentials, proving that there are no shorts or leaking of the slurries, we have been unable to obtain current-voltage data that agrees with standard data for the relevant active materials or with the results reported in [1].

**Mechanistic studies of the tin-bromine system for redox flow batteries**

The Bard group is focusing first on tin-based systems for redox flow batteries. Tin(IV) bromide is a promising candidate because both redox couples, Sn(IV)/Sn(II) and Br₂/Br⁻ are dissolved in same solution, eliminating concerns of cross contamination. The system has been limited by poor electrochemical reversibility of Sn(IV)/Sn(II). With a view toward discovering ways to improve that, progress is being made toward a complete understanding of the mechanism of the Sn(IV)/Sn(II) redox reaction. A key question has been whether (1) two electrons are simultaneously transferred through tunneling interface or (2) each stepwise one-electron transfer via a Sn(III) intermediate is preferred reaction pathway. Jinho Chang has now detected the Sn(III) intermediate through two electrochemical analysis methods, fast scan cyclic voltammetry and scanning electrochemical microscopy (SECM). Furthermore, a rate constant for the disproportionation of Sn(III) was estimated from a collection efficiency measured in SECM.[4]

**Pure liquid reactants for redox flow batteries**

Redox flow batteries tend to have relatively low specific energy density. For example, the energy density of a vanadium redox flow battery is 25-35 Wh/kg. Energy density is related to the concentration of redox species in solution. In the case of an all-vanadium redox flow cell, the maximum concentration of the vanadium ion is ~ 2 M in sulfuric acid solution. Sn(IV)/Sn(II) is a promising redox couple for flow batteries in part because it transfers two electrons. Sn(IV)Cl₄ is a special case among tin halides because it is liquid at room temperature. Potentially, it could be used as a redox electrolyte without dilution (Sn concentration is ~ 8.5 M). Pure liquid Sn(IV)Cl₄ has low conductivity (dielectric constant, εᵣ = 3.014), so its electrochemistry had not been reported. The Bard group is now working on the first studies of the electrochemistry of Sn(IV)Cl₄ liquid, both undiluted and in solution with dichloromethane, as the first step in studying the metal halide liquid redox flow battery.[5] Challenges include passivation due to bulk precipitation of Sn(II)Cl₂, and iR drop due to low conductivity.
Progress

We expect that the fundamental leaps in chemistry, materials, and engineering knowledge provided by this work will unlock the ability to build and operate commercial grid-scale storage for intermittent renewable energy sources. This type of large-scale storage is a natural complement to intermittent renewable generation methods, and to the degree we can enable those methods, we can directly reduce greenhouse gas emissions.

Our initial modeling effort, which is nearly complete, will provide a basis for understanding whether a slurry concept can deliver the required cost per kWh for grid storage applications. We should be able to provide key material figures of merit for considering a slurry system versus a true electrolyte-based flow battery concept. This modeling effort should be complete by late May.

Future Plans

We seek to accomplish the following: (1) synthesize new ligands and complexes as electrolytes with tailored thermodynamic potentials, (2) screen these candidate materials under a variety of conditions on carbon electrodes, (3) characterize the most promising materials in larger electrochemical cells, (4) quantify the transport properties of ionomeric membranes in the presence of redox couples and supporting electrolyte, (5) test and simulate candidate systems as a means of down-selecting lab-scale tests to understand performance issues, (5) develop transient models based on conservation principles, incorporating the fundamental modes of transport for the charged species and solvent, including transport and reaction kinetics to simulate the performance of various RFB systems, and (7) facilitate the design of large-scale (>10 MW, and on the order of 1 GWh) RFB systems.

References


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Abstract
This project has as its primary focus the development of understanding of relevant properties of membranes and separators and other materials used in redox flow batteries (RFBs), with specific emphasis on the Vanadium Redox Battery (VRB). This will lead to an understanding of development needs and directions for materials in flow batteries. In this first phase of the activity, we have started the development of a number of experimental methods, together with their appropriate analytical framework, to measure uptake of species into membranes and their transport. To frame this issue, a membrane used in a VRB is exposed one each side to a concentrated aqueous acid (typically sulfuric) solution containing vanadium species in at least 2 of 4 oxidation states. The concentrations are such that several things happen in the membrane:
1. Acid is imbibed into the membrane.
2. Water is ejected from the membrane
3. Vanadium species enter the membrane from each side.
Also, substantial water can move across membranes in an operating cell.

To describe uptake and transport in such a system, we have developed a suite of measurement methods: These measurements allow:

i. Determination of acid and water uptake into the membrane from bathing solutions of sulfuric acid in water.
ii. Determination of vanadium uptake into the membrane.
iii. Determination of vanadium and other species transport across a membrane. This is critical because of the effect of cross-over and water transfer on capacity fade and cell unbalancing in the device.
iv. Determination of conductivity of membranes exposed to solutions of sulfuric acid in water, including the effects of adding vanadium ions.

In addition, a number of qualitative observations were made concerning net water transport through the membranes during transport experiments.
Primary results include (i) the finding that significant acid uptake into the membrane occurs at concentrations of external solution typical of a flow battery, that this acid uptake is associated with dehydration of the membrane and decreased conductivity; (ii) our new EPR-detection method shows that significant cross-over of vanadium species occurs and allows us to directly quantify the rate; (iii) water transport across the PFSA membrane is substantial and can lead to an unbalanced cell. Finally, an initial suite of methods for characterizing transport in these cells is now in hand, a primary objective of this first partial year of work.

Introduction
This project has as its primary focus the development of understanding of relevant properties of membranes and separators and other materials used in redox flow batteries (RFBs), with specific emphasis on the Vanadium Redox Battery (VRB). Our emphasis is oriented toward two goals: (1) supporting the activities of Prof. Meyers at UT-Austin by providing experimental data on transport of species in the battery materials as a function of composition, suitable for use in models; and (2) using this same data to draw conclusions concerning ‘best’ material approaches to improve on several aspects of VRB performance.

Background
During the past year, redox flow battery development efforts have proliferated worldwide. Most of these efforts are focused on developing commercial products. Projects like ours, which seek to provide the underpinnings for improvement of components leading to cost reduction and performance enhancement, are less common. Much of what has been done on vanadium redox batteries prior to the last year has lacked rigor. An additional development in our labs at UTK, predating and not covered under the GCEP activity, has focused on improving power density of the VRB via cell design and control of mass transport in electrode materials. This has led to roughly an order of magnitude improvement relative to reliable published data. We can currently operate a VRB cell at a peak power density exceeding 1 W/cm². This cell design is available for our use in testing materials such as membranes, the primary focus of our GECP activity.

Results
In this first phase of the activity, we have started the development of a number of experimental methods, together with their appropriate analytical framework, to measure uptake of species into membranes and their transport. To frame this issue, a membrane used in a VRB is exposed one each side to a concentrated aqueous acid (typically sulfuric) solution containing vanadium species in at least 2 of 4 oxidation states. The concentrations are such that several things happen in the membrane:

1. Acid is imbibed into the membrane.
2. Water is ejected from the membrane
3. Vanadium species enter the membrane from each side.

Also, substantial water can move across membranes in an operating cell.

To describe uptake and transport in such a system, we need to develop quantitative methods to determine the water, acid and vanadium content in the membrane as well as
the oxidation state(s) of the vanadium, all as a function of concentration of the solution to which the membrane is exposed. We then need to determine transport rates of species under the same conditions. This is truly a daunting task. The transport of the individual species is coupled to that of other species.

Accordingly, we have broken the overall large measurement problem down into a series of simpler measurements and started to develop methods for obtaining accurate subsets of data. These measurements are:

i. Determination of acid and water uptake into the membrane from bathing solutions of sulfuric acid in water.
ii. Determination of vanadium uptake into the membrane, one oxidation state at a time, from solutions.
iii. Determination of vanadium and other species transport across a membrane, one species at a time. This is critical because of the effect of cross-over and water transfer on capacit fade and cell imbalancing in the device.
iv. Determination of conductivity of membranes exposed to solutions of sulfuric acid in water, including the effects of adding vanadium ions to the sulfuric acid solutions (and thus into the membranes).

In addition, a number of qualitative observations were made concerning net water transport through the membranes during transport experiments.

For this initial work, the membrane employed was typically Nafion or another PFSA. In what follows, we describe the specific methods and results for each of the aforementioned studies. Our emphasis here is on creating validated methods and preliminary analysis of the physical chemistry associated with the results.

A. Acid and Water Uptake
Acid and water uptake into the membrane were determined in the following manner. A membrane sample was immersed in a solution of sulfuric acid in water of a given concentration. The membrane was removed after equilibration, surface-blotted, weighed and then immersed in pure water. This serves to extract acid into the water. After the membrane was removed, the solution is titrated to determine the acid content. The membrane is dried and weighed. A simple mass balance then reveals water and acid contents in the equilibrated membrane. In Figure 1, we show the results of this experiment for several different Nafion forms.
As seen in the figure, the results are broadly consistent independent of the membrane thickness. The water content drops with acid concentration of the immersion solution. Acid uptake, expressed as moles of acid per mole of fixed site in the membrane, increases with increase molality, leveling off above 10 m acid solution. Generally speaking, we observe dehydration of the membrane as the water activity in the equilibration solution decreases, highlighted in figure 2, and acid uptake into the membrane, shown in Figure 3. The dehydration effect is in qualitative agreement with previous observations from equilibration of PFSA membranes with water in the vapor phase. Quantitatively, the uptake at the all water activities is somewhat higher than expected based on activity. This is partly due to the liquid phase equilibration and probably partly due to the water associated with the acid in the membrane. Equilibration of a membrane with pure liquid water under such conditions yields a higher water uptake than that observed with the pure vapor, reflected in the data in figure 2 at higher activities.
Above a concentration of roughly 0.4M, Donnan exclusion of acid breaks down and acid is imbibed by the membrane. The thinner membranes appear to take up slightly more acid at high concentration of acid in solution. We have ascribed this to a possible surface adsorption effect and modeled it quantitatively.

**B. Vanadium uptake**

It is obvious that vanadium species are taken into the membrane. The membrane becomes colored upon exposure to vanadium. A surprising result was obtained when we analyze the vanadium oxidation state in the membrane. Based on analysis of EPR spectra of membranes exposed to solutions ex situ or in a battery, it appears that almost all vanadium in the membrane is present as vanadium (IV), VO$^{3+}$. We are developing further methods to systematically quantitate vanadium partitioning into the membrane.
**C. Vanadium Transport**

To measure vanadium transport, we are developing and implementing two methods. First, we are acquiring a standard diffusion cell, with two compartments separated by a membrane, to allow transport. In a second configuration, shown in Figure 4, we are using a standard test cell to determine vanadium cross-over with and without current. In this case, our detector is an EPR instrument. EPR active species are obtained from V(II) and V(IV). We can access other oxidation states (V(III) and V(V)) by quantitatively converting these species in the effluent into V(II) and V(IV). Typical V(II) and V(IV) signals are shown in Figure 5. We have constructed a flow-through cell to feeding solution on the receiving side of the membrane into the instrument. The EPR is a highly sensitive detector and allows us to detect relatively minute rates of transport.

Several significant issues arise related to obtaining meaningful transport data in any experiment. First, the concentrated solutions typically used in the VRB yield an extremely complex transport problem. In principle, we would need to determine 21 independent transport coefficients describing pure species transport plus all needed pairwise coupling coefficients. Second, it is virtually impossible to isolate a single transported species. Indeed, substantial water transport is observed in any diffusion experiment.

To mitigate these factors, we are taking several steps. First, we are ruthlessly simplifying our experiments. We are looking at transport of one vanadium species at a time. We also are developing a systematic framework, based on non-equilibrium thermodynamics, to assess these simplifications. Some initial work was carried out, in the manner of the literature, to suppress the water transport across the membrane by maintaining a constant ionic strength on each side of the membrane through the additional of MgSO₄ to the ‘receiving’ side of the membrane. However, this adds further complexity because Mg²⁺ can likely partition into the membrane.

![Figure 4: Schematic of Transport Measurements using EPR Detection](image)
Generally speaking, we are developing the analytical chemistry methodology needed to carry out determinations of the full mass balance for these transport measurements.

In Figure 6, we show some typical results of transport studies using the method sketched in Figure 4, carried out for dilute feed solutions. As is shown in Figure 7, the signal grows over a period of roughly 10 hours. This data yields a permeability of roughly $3 \times 10^{-6}$ s/cm based a simple single component exponential model.
Figure 7: EPR signal intensity for V(IV) cross-over vs. time
D. Conductivity Studies

The membrane conductivity in a VRB is lowered relative to that in a fuel cell, for example, in which the membrane is exposed to water vapor. It is critical to achieving high performance to maintain the maximum achievable level of membrane conductivity while simultaneously keeping cross-over to an acceptable level. Several factors influence the conductivity. These are the membrane water and acid content and the partitioning of vanadium species into the membrane.

In this piece of work, we try to disentangle these various effects. In Figure 8, the membrane conductivity vs. solution composition is shown for several PFSA membranes. Each membrane exhibits a slight initial increase in conductivity as acid concentration is increased followed by a sharp decrease at the highest acid concentrations. The conductivity when exposed to ~5 or 6 m acid solutions is of significance since this is the approximate acid concentration used in practice. Roughly a factor of 2 decrease in conductivity is observed for Nafion 117 relative to the same membrane in pure water. To put this into perspective, this loss corresponds to roughly 150 mV extra loss due to membrane iR in cell operating at 1 A/cm², a >10% efficiency loss in the cell.

![Graph showing conductivity of various membranes](image)

Figure 8: Conductivity of Various Membranes Exposed to Sulfuric Acid Solutions vs. Acid Concentration

As noted above, the membrane loses water and takes in acid upon exposure to the solutions. The loss of water is an osmotic effect, resulting from the decrease in water activity as a function of acid concentration. Figures 9 and 10 show the conductivity data recast as functions of water activity and water content respectively. Clearly, the conductivity decreases as a function of water content, driven by the lowering of water activity.
In Figures 11 and 12, we show data that reveal the influence of vanadium uptake into the membrane. As noted above, V(IV) is the primary species observed to be present in the membrane. Therefore, we focused on this species.
Figure 11 indicates a substantial loss in membrane conductivity as the concentration of VO$^{2+}$ in solution is increased toward the practical value of roughly 2M. We note that the conductivity for the highest concentration shown here is roughly 3X lower than that of pristine Nafion, entailing a loss of roughly 300 mV extra loss due to membrane iR in a cell operating at 1 A/cm$^2$, a $>20\%$ efficiency loss in the cell.

To understand what membrane properties might need to be altered to partially or fully mitigate this situation, we began to study partitioning into the membrane under conditions in which no excess acid is imbibed into the membrane. Figure 12 shows resulting conductivity of dilute solutions. The message here is clear: in the PFSAs, vanadium competes very effectively with protons for ion exchange sites in the polymer.
Progress
In this initial phase of the project, we have developed and deployed a series of experimental methods to study the needed composition and transport properties of membranes under conditions used in VRBs. This is a necessary first step in the direction of our ultimate goal of providing clear insight into rational direction for development of improved materials. The work is at present still evolving. In the process of developing our suite of methods, we have become acutely aware of the breadth of information required to completely tackle this situation as well as the relative lack of careful experimentation report in the open literature. Though a number of publications have appeared that discuss similar issues, none is as systematic as we feel is necessary. Often, more than 2 variables are simultaneously altered in experiments. Another source of issues with the literature is the partial description of composition in many cases. It is unfortunately nearly impossible to isolate key factors with the current state of the issue.

Future Plans
Our future efforts will continue the development of test methods and begin to apply these to a wider range of membranes. In particular, we expect to test the aspects reported above on additional PFSA membranes as well as on hydrocarbon membranes. Also, we will implement these membranes into cells and carry out a limited amount of performance testing, deploying our advanced cell and electrode designs.

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